

# PATENT SPECIFICATION

974,164

DRAWINGS ATTACHED.

Date of Application and filing Complete Specification :  
March 29, 1961. No. 11470/61.

Application made in United States of America (No. 19392)  
on April 1, 1960.

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Index at Acceptance :—C2 C(1G5B, 1G6B2, 1G6B5).

International Classification :—C 07 d.

## COMPLETE SPECIFICATION.

### Production of Epichlorohydrin.

We, PITTSBURGH PLATE GLASS COMPANY, 55° C., thereby stripping the epichlorohydrin, produced in the reaction medium, from 45  
the reaction medium as a gaseous mixture

#### CORRECTION OF CLERICAL ERRORS

#### SPECIFICATION NO. 974,164

The following correction is in accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated the 11th day of February, 1965

Page 1, line 73, after "Thus" delete "is"

Attention is also directed to the following printer's errors:—

Page 2, line 41, for "recourse" read "recourse"

Page 4, line 59, for "equeous" read "aqueous"

Page 4, line 98, for "ligher" read "lighter"

THE PATENT OFFICE,  
22nd April, 1965

D 037562/4/200

30 MINIMIZED... high yields are the various side reactions and amounts of by-products. An aqueous mixture of two dichlorohydrin isomers (as are obtained in hypochlorination of allyl chloride) is converted with facility to epichlorohydrin.

35 According to the present invention there is provided a process for the production of epichlorohydrin in the form of a mixture thereof with water vapour, from which mixture epichlorohydrin may be separated, which comprises treating with steam, an aqueous reaction medium which is provided by mixing an inorganic alkali hydroxide, 40 water and dichlorohydrin, said reaction medium immediately prior to said steam treatment being at a temperature of below

hydrin-water azeotrope notably in water 50 per cent water by weight of the two. Thus is, in the performance of the present invention, a total condensate of the stripped gas mixture of water vapour and epichlorohydrin contains upwards of 50 per cent by weight of water based on its water and epichlorohydrin content. 75

More particularly, the aqueous mixture of dichlorohydrins and inorganic alkaline hydroxide is contacted with live steam and promptly elevated to an appropriate reaction temperature while epichlorohydrin is stripped from the reaction medium in which it is formed. Thus, epichlorohydrin is removed promptly from solution in the 85

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## COMPLETE SPECIFICATION.

### Production of Epichlorohydrin.

We, PITTSBURGH PLATE GLASS COMPANY, a Corporation organised under the laws of the State of Pennsylvania, United States of America, of One Gateway Center, Pittsburgh, Pennsylvania, United States of America, (Assignee of FRED CLYDE TRAGER), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of epichlorohydrin.

Epichlorohydrin is an important raw material in the manufacture of the epoxide resins, e.g., glycidyl ethers of mono- or polyhydric compounds. Thus, epichlorohydrin and 2,2-bis(4-hydroxyphenyl) propane (Bisphenol A) are reacted as principal components in well known and widely used epoxide resins. Synthetic glycerol may also be readily prepared from epichlorohydrin.

It has now been found possible to efficiently convert dichlorohydrins to epichlorohydrin with high yields and conversions. Minimized substantially to provide these high yields are the various side reactions and amounts of by-products. An aqueous mixture of two dichlorohydrin isomers (as are obtained in hypochlorination of allyl chloride) is converted with facility to epichlorohydrin.

According to the present invention there is provided a process for the production of epichlorohydrin in the form of a mixture thereof with water vapour, from which mixture epichlorohydrin may be separated, which comprises treating with steam, an aqueous reaction medium which is provided by mixing an inorganic alkali hydroxide, water and dichlorohydrin, said reaction medium immediately prior to said steam treatment being at a temperature of below

55° C., thereby stripping the epichlorohydrin, produced in the reaction medium, from said reaction medium as a gaseous mixture comprising water vapour and epichlorohydrin, the temperature of said gaseous mixture being stripped from the reaction medium being above the normal boiling point of the water-epichlorohydrin azeotrope, said gaseous mixture having a water vapour content which is at least 50% by weight of the water vapour and epichlorohydrin, the water vapour content being determined by the amount of steam admitted.

In the present invention dichlorohydrin, especially mixtures of dichlorohydrin such as are obtained by the hypochlorination in aqueous media of allyl chloride, are reacted with aqueous inorganic alkali hydroxide to prepare epichlorohydrin. Thus, in the present invention, an aqueous mixture of dichlorohydrin (one or both isomers) and inorganic alkaline hydroxide are subjected to the action of steam and epichlorohydrin is stripped from such mixture as a gaseous mixture of epichlorohydrin and water vapour which has a water vapour content in excess of the water content of the epichlorohydrin-water azeotrope notably in excess of 50 per cent water by weight of the two. Thus is, in the performance of the present invention, a total condensate of the stripped gas mixture of water vapour and epichlorohydrin contains upwards of 50 per cent by weight of water based on its water and epichlorohydrin content.

More particularly, the aqueous mixture of dichlorohydrins and inorganic alkaline hydroxide is contacted with live steam and promptly elevated to an appropriate reaction temperature while epichlorohydrin is stripped from the reaction medium in which it is formed. Thus, epichlorohydrin is removed promptly from solution in the

aqueous alkaline hydroxide reaction medium as a component of a gas stream which is at a temperature above the normal boiling point of the water-epichlorohydrin azeotrope, preferably above 96° C. and below 100° C.

A still further feature of the present invention is its performance in the conversion of the respective isomers of the dichlorohydrin into epichlorohydrin. Hypochlorination of allyl chloride in aqueous medium results in two isomers of glycerol dichlorohydrin, namely 2,3-dichloropropane-1-ol and 1,3-dichloropropane-2-ol, usually in the weight proportions of about two parts of 2,3-isomer per part of 1,3-isomer. Other isomer ratios of the two glycerol dichlorohydrin isomers include ratios as high as five parts of the 2,3-isomer per part of the 1,3-isomer and often as low as one part of the 2,3-isomer per two parts of the 1,3-isomer. Of the two isomers, the 1,3-isomer apparently converts to epichlorohydrin with greater ease than the other, or at least appears to react more rapidly.

In preferred embodiments of the present invention, rapidly formed epichlorohydrin (probably epichlorohydrin obtained from conversion of the more reactive 1,3-isomer) is removed from solution with aqueous alkali metal hydroxide by the action of steam stripping while the water soluble less volatile dichlorohydrins and especially the less reactive 2,3-isomer are maintained at conditions conducive to formation of epichlorohydrin. As further epichlorohydrin forms, it too is stripped by steam and removed from an environment which degrades the product. Those conditions conducive to effective epichlorohydrin production are best provided by recourse to a vertical column (preferably packed with inerts) as the reactor. In the operation of the column, the reactants (dichlorohydrins and alkali hydroxide) are introduced usually as an aqueous mixture into the column between its extremities, normally in the upper portion. Below this, and usually at its lower extremity, live steam is fed to the column. From the lower extremity of the column, aqueous liquid material preferably lean in dichlorohydrin is withdrawn. The salt formed by the reaction, e.g., sodium chloride or calcium chloride also leaves the system with this liquid. Out of the column, usually as overhead, a gas mixture of epichlorohydrin and water vapour is removed. This mixture is condensed into a phase separable system having an aqueous phase and an organic epichlorohydrin rich phase.

The respective rates of feed (steam and reactants), column length and other variables are so correlated that the liquid effluent from the lower portion of the column

contains a minimum of unreacted dichlorohydrins, notably less than about 1 per cent by weight of the underflow, while the overhead (or vapours removed from the zone of the column above where the reactants are introduced) is predominantly water.

Moreover, the gaseous mixture of epichlorohydrin and water vapour removed from the zone of reaction (and normally withdrawn from the column as the product removal means) is at a temperature above the normal boiling point of the water-epichlorohydrin azeotrope (89° C.) and preferably is above 96° C. but below 100° C., ideally 97° C. to 98° C.

The temperatures prevailing in the column between the zone of steam introduction and removal of product containing vapours are usually between 90° C. and 110° C. Ideally, the column is operated at a substantial constant temperature of around 97° C.

Established in the packed tower reactor are conditions giving rise to an upwardly flowing stream of water vapour containing progressively more epichlorohydrin and a downwardly flowing aqueous stream which becomes progressively leaner in dichlorohydrin. As the reactants enter the column, a liquid mixture thereof is promptly raised to temperatures effective for conversion of the dichlorohydrin to epichlorohydrin by the rising steam stream. This steam also strips epichlorohydrin from the liquid reaction medium. As above explained, the 1,3-dichlorohydrin isomer reacts with greater facility and under less rigorous conditions than the 2,3-dichlorohydrin isomer. Accordingly, the aqueous stream descending in the column initially becomes relatively lean in the more reactive 1,3-dichlorohydrin isomer through its conversion to epichlorohydrin. As this liquid alkali hydroxide stream descends downwards, reaction of the 2,3-dichlorohydrin occurs to an increasing extent and the dichlorohydrin content of the descending aqueous stream becomes well depleted in dichlorohydrin content. Ultimately and under ideal conditions, underflow from the column reactor is substantially free of unreacted dichlorohydrins.

The conversion of glycerol dichlorohydrins (both isomers) occurs by reaction with an aqueous alkali, notably alkali metal hydroxide. Suitable alkali hydroxides include alkaline earth metal hydroxides such as calcium hydroxide and alkali metal hydroxides such as sodium hydroxide. When the alkali hydroxide is water insoluble or sparsely water soluble, it is present in the reaction mixture as an aqueous slurry while water soluble alkali hydroxides such as sodium hydroxide are present as aqueous solutions.

It is best to establish an aqueous medium containing the reactants just before their

- ture of approx. 25° C. to the upper portion of reactor column 2 provided by a vertically disposed glass tower 30 centimetres high, having an internal diameter of 47 millimetres and packed with 0.25 inch Beryl saddles. This column was jacketed and maintained at an essentially constant temperature by circulation in the jacket of a heated aqueous solution of glycerol.
- Also mixed with the aqueous sodium hydroxide solution and fresh feed were the recycled aqueous phases, containing glycerol dichlorohydrins from those portions of the process hereinafter detailed, the recycled aqueous phases being at a temperature of 20° C.
- Water was heated and vaporized at the rate of 20 cubic centimetres per minute under atmospheric conditions into steam and this steam was introduced into the lower portion of the reactor.
- With these feeds to the column, dichlorohydrin was converted by reaction with the aqueous alkali hydroxide to form epichlorohydrin, the steam supplying heat to establish the suitable reaction temperature (of about 95° C. to 100° C.) and to strip away from reactive contact with the aqueous alkali reaction medium epichlorohydrin as it is formed. In this fashion, epichlorohydrin is recovered as overhead from the column reactor in a gas stream of water vapour and epichlorohydrin. Some glycerol dichlorohydrin (one or both isomers, although usually the 2,3-isomer) plus contaminants (e.g. trichloropropane) are present in the fresh dichlorohydrin feed. The amount of heat supplied to the reactor by virtue of the steam (and possibly by the jacket) maintains the temperature of the overhead gas stream as it leaves the column at the value indicated in the table, notably above 96° C. but below 100° C.
- This overhead was totally condensed in condenser 5 by cooling to a temperature of 20° C., and the resulting liquid mixture is then phase separated in separator 6. Water obtained from the subsequent drying step (which will hereinafter be described) is also present in the mixture.
- The lighter aqueous phase was recycled for admixture with the aqueous sodium hydroxide and fresh dichlorohydrin solutions which are introduced as a mixture into the upper portion of the reactor column. Water soluble components of the overhead vapours from the reactor including dichlorohydrin and epichlorohydrin are present in this aqueous phase so explaining the reason for the recycle.
- The organic phase was then fed to an intermediate portion of drying column 7 which was 28 centimetres high, having an internal diameter of 10 millimetres and packed with 0.625 inch glass helices operated at a bottom temperature of about 100° C. and atmospheric pressures. In this column the crude epichlorohydrin was dried, e.g., the small amount of water not removed by the prior phase separation was separated. Epichlorohydrin vapours emanating as overhead from this drying column take with them water vapour (thus drying the balance of the epichlorohydrin) and are returned to the total condensate from the reactor column as indicated in the schematic diagram.
- The underflow from the drying column (substantially dry epichlorohydrin) was fed to an intermediate portion of product column 12 provided by a vertical tube 28 centimetres high, having an internal diameter of 16 millimetres and packed with 0.625 inch glass helices. This column is operated with a bottom temperature of 117° C., and an overhead gas temperature of 114° C. to 116° C. Overhead vapours were totally condensed and condensate collected at the rate of 2 cubic centimetres per minute of high purity epichlorohydrin.
- Underflow from column 12 comprising materials boiling above that of epichlorohydrin, notably organics, was removed, mixed with 6 cubic centimetres of water per minute and 6 centimetres per hour of trichloropropane. The resulting composition was phase separated, the heavier organic phase being discarded and the lighter aqueous phase being recycled for admixture with fresh reactants and introduction into the reactor column.
- The following table summarizes the continuous operation of the above procedure in the production of epichlorohydrin according to several runs.

TABLE.

	Run	Run Duration (hours)	Reactor Overhead Vapour Temperature °C.	Weight Ratio Overhead Vapours Water-Epichlorohydrin	Per Cent Yield (based on dichlorohydrin fed)
110	A	5	98	9:1	92.1
	B	8	97.2	9:1	92.7
	C	8	99.1	9:1	90.2
	D	4	95-96	9:1	89.5
115	E	5	100.8	9:1	86.5

introduction into the column. This may be done by mixing aqueous solutions or slurries of the respective reactants immediately prior to the introduction. When the alkali hydroxide is water soluble, combining the respective streams of reactants in a "T" tube suffices. However, with calcium hydroxide or like water insoluble materials, it is better to feed the materials to a stirring zone.

Whatever expedient is employed in the preparation of the reaction medium, it is best to minimize epichlorohydrin formation in the resulting mixture prior to its entry in the reactor column. To this end, temperatures of the mixture prior to such introduction are kept below 55° C. and most conveniently at 25° C. In addition, once formed, the reaction mixture is promptly forwarded to the column.

Ideally, liquid underflow from the column is substantially free of dichlorohydrin while vapours removed from the upper end of the column are also ideally free of dichlorohydrin. Nevertheless, practical conditions frequently are such that the liquid effluent from the lower portion of the column may contain up to 1 per cent by its weight of dichlorohydrin. Similarly, a significant percentage of dichlorohydrin may accompany product in water vapour which leaves the column.

Dichlorohydrin present in the water vapour removed from the upper portion of the reactor may be recovered and recycled for conversion to epichlorohydrin. Thus, dichlorohydrin in the withdrawn product stream may be recovered by condensing the epichlorohydrin-water vapour mixture, phase separating the aqueous phase in which the dichlorohydrin is present and recycling such aqueous phase, for example, as part of the dichlorohydrin source which is mixed with the alkali hydroxide for feed to the column.

The separated organic phase comprising crude epichlorohydrin product may be further purified, in the manner hereinafter detailed more completely in the example, or by other expedients.

Performance of a specific embodiment of the present invention is best understood by reference to the accompanying drawing which is a schematic flow sheet of a typical process herein contemplated.

As shown in the flow sheet, an aqueous solution of sodium hydroxide and an aqueous solution of one or both isomers of glycerol dichlorohydrin are mixed at 1. A portion of the aqueous dichlorohydrin solution may be provided by recycling aqueous media containing dichlorohydrin values obtained from various stages of the process, as will hereinafter be specifically illustrated. The resulting mixture is then introduced into

the uppermost portion of jacketed column 2 packed with Beryl saddles or other inert column packings. At a lower extremity (or level) 3 of the reactor live steam is introduced. In the operation of the column reactor 2, underflow is continuously removed. This underflow is principally comprised on a weight basis of water and sodium chloride or a chloride salt having an anion corresponding to the anion of the alkali hydroxide.

Product epichlorohydrin is withdrawn as a gaseous overhead comprised principally of epichlorohydrin vapours and water vapour from an upper portion of the column above the level at which the reaction mixture is introduced, condensed in condenser 5 and phase separated in separator 6. The lighter aqueous phase (containing some dichlorohydrin) is recycled to provide a portion of the dichlorohydrin fed to the system. The heavier organic phase comprising crude epichlorohydrin is fed to an intermediate portion of a drying column 7, the overhead water vapour which is condensed in condenser 8 and recycled if desirable to comprise a portion of the dichlorohydrin requirements fed to reactor 2. Thus, in column 7, moisture or small amounts of water are removed from the crude epichlorohydrin. Along with the water, minor amounts of dichlorohydrin may also be removed.

Underflow from drying column 7 comprising substantially anhydrous crude epichlorohydrin is then fed to an intermediate zone of finishing column 12. After condensing in condenser 11, high purity liquid epichlorohydrin is obtained. Underflow from finishing column 12 is mixed with water and then trichloropropane in mixer 9. The resulting mixture is separated in phase separator 10 into its organic constituents and its aqueous component which may be recycled as a source of dichlorohydrin for preparing the reaction mixture.

The present invention may be illustrated by, but is in no manner limited to the following example.

#### EXAMPLE.

Epichlorohydrin was produced continuously over durations indicated in the table given below by the method illustrated schematically in the drawing. In the procedure, 19 cubic centimetres of an aqueous sodium hydroxide solution containing 10 per cent sodium hydroxide and 16 per cent sodium chloride by weight was mixed with 100 grams per minute of an aqueous glycerol dichlorohydrins solution containing 3.5 per cent by weight of the glycerol dichlorohydrins (65 parts 2,3-dichloropropane-1-ol to 35 parts 1,3-dichloropropane-2-ol by weight) and the resulting mixture fed at a tempera-

In Runs C and E, a slight superatmospheric pressure was supplied by a nitrogen pad.

The concentration of alkali hydroxide and dichlorohydrin fed to the reactor is widely variable. Usually, the concentration of dichlorohydrin (either or both isomers) is limited by the solubility of such dichlorohydrin in the aqueous media fed to the reactor. As a rule, these dichlorohydrin concentrations are above 2 per cent but below 12 per cent by weight. Alkali hydroxide concentrations are in general governed principally by operating conveniences, such as the avoidance of too concentrated and hence unmanageable liquid medium due to high hydroxide concentrations.

The conversion of dichlorohydrin to epichlorohydrin in accordance herewith consumes one mole of sodium hydroxide per mole of epichlorohydrin formed or mole of dichlorohydrin reacted. Using calcium hydroxide, only a half mole of the hydroxide per mole of the dichlorohydrin is consumed. Sufficient alkali hydroxide is provided in the reaction mixture to provide for substantially complete conversion of the dichlorohydrin to epichlorohydrin in the reactor. That is, one equivalent of metal hydroxide per equivalent of dichlorohydrin is used.

#### WHAT WE CLAIM IS:—

1. A process for the production of epichlorohydrin in the form of a mixture thereof with water vapour, which comprises treating with steam, an aqueous reaction medium which is provided by mixing an inorganic alkali hydroxide, water and dichlorohydrin, said reaction medium immediately prior to said steam treatment being at a temperature of below 55° C., thereby stripping the epichlorohydrin, produced in the reaction medium, from said reaction medium as a gaseous mixture comprising water vapour and epichlorohydrin, the temperature of said gaseous mixture being stripped from the reaction medium being above the normal boiling point of the water-epichlorohydrin azeotrope, said gaseous mixture having a water vapour content which is at least 50% by weight of the water vapour and epichlorohydrin, the water vapour content being determined by the amount of steam admitted.

2. A process as claimed in Claim 1 in which the temperature of said gaseous mixture being stripped from the reaction medium is above 96° C. but below 100° C.

3. A process as claimed in Claim 1 or

2 in which the temperature of said gaseous mixture being stripped from the reaction medium is from 97° C. to 98° C.

4. A process as claimed in any of Claims 1 to 3 in which the aqueous reaction medium is fed to an intermediate level of a vertical column, steam is introduced into the column at a level below said intermediate level and a gaseous mixture of water vapour and epichlorohydrin is withdrawn from a level above said intermediate level.

5. A process as claimed in any of the preceding claims in which the gaseous mixture is condensed to form a condensate containing 9 parts of water per part of epichlorohydrin by weight.

6. A process as claimed in any of the preceding claims in which the aqueous reaction medium immediately prior to steam treatment is at a temperature of 25° C.

7. A process as claimed in any of Claims 1 to 6 in which there is sufficient inorganic alkali hydroxide in the aqueous reaction mixture to substantially completely convert the dichlorohydrin to epichlorohydrin.

8. A process as claimed in any of Claims 1 to 7 in which the inorganic alkali hydroxide is an alkali metal hydroxide.

9. A process as claimed in any of Claims 1 to 7 in which the inorganic alkali hydroxide is an alkaline earth metal hydroxide.

10. A process as claimed in any of Claims 1 to 9 in which the gaseous mixture of epichlorohydrin and water vapour comprising also dichlorohydrin is condensed, phase-separated into an aqueous phase containing dichlorohydrin and an organic phase, and the aqueous phase recycled as part of the dichlorohydrin source for forming the aqueous reaction medium.

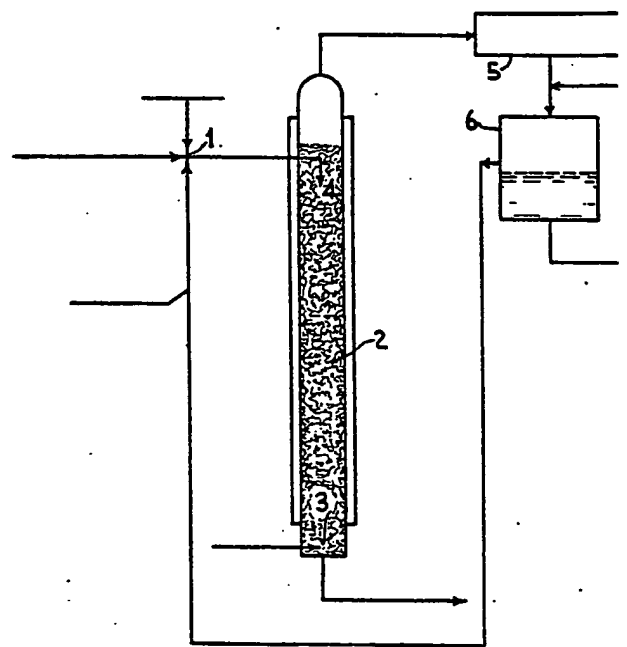
11. A process for the production of epichlorohydrin which comprises separating epichlorohydrin from said epichlorohydrin-water vapour mixture produced according to any of Claims 1 to 9.

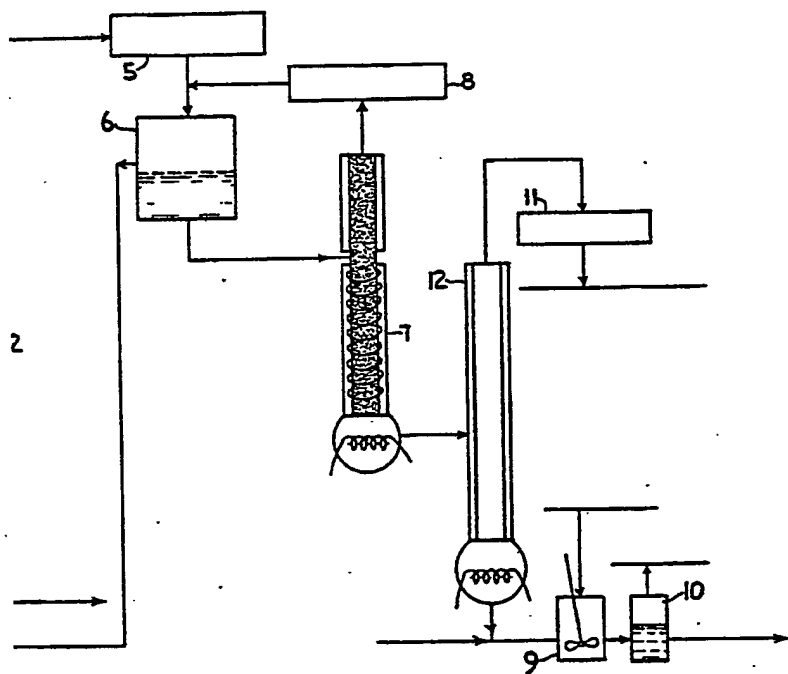
12. A process for the production of epichlorohydrin substantially as hereinbefore described with particular reference to the foregoing examples and as illustrated in the accompanying drawing.

13. An epichlorohydrin-water mixture whenever obtained by a process as herein described and claimed.

14. Epichlorohydrin whenever obtained by a process as herein described and claimed.

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574184 COMPLETE SPECIFICATION  
1 SHEET  
This drawing is a reproduction of  
the Original on a reduced scale

